

fired at 1200° C. in a muffle furnace overnight. The solid was again surface-treated by the method described in this paragraph, to give a glass-coated alumina.

#### EXAMPLE 7

Spray-dried biologically active glass powder was made from: Solution I—68.3 g of calcium formate—7.3 g of sodium formate—enough water to give 600 ml of solution. Solution II—190.2 g of 37.1% Na<sub>2</sub>O, 3.38 g of SiO<sub>2</sub>—38.5 g of Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O and enough water to give 600 ml of solution. Additional solutions were prepared until 4 liters of each had been made.

To 720 ml of Solution I and 100 ml of formic acid in a blender cup was added 720 ml of Solution II with vigorous stirring. This final solution was then spray-dried.

A 3 necked round bottom flask was fitted with a paddle stirrer and a N<sub>2</sub> inlet tube, and was heated with a Meeker burner. About 25 g of the spray-dried powder was placed in the nitrogen-purged flask, the stirrer was started and the burner was turned on. The powder stuck together as liquids began to distill from the flask. On continued heating, the particles became free flowing and at 380° C., they degassed vigorously liberating a flammable gas, probably CO and H<sub>2</sub>. More spray-dried material was added at such a rate that agglomeration did not occur. Over 35 min, 320 g of spray-dried material was added. The stirred solid was heated to 520° C. and cooled. The experiment required 45 min and gave 210 g of brown free-flowing powder. When heated to 950° C. in air, the product became a white friable cake that was easily crushed to powder with mortar and pestle.

#### EXAMPLE 8

This Example represents a single solution method for making biologically active glass and/or glass-coated support particles. In 15 ml of H<sub>2</sub>O was dissolved 1.6 g of Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O. To that solution was added 7.9 g of a 37.1% aqueous solution of Na<sub>2</sub>O·3.38SiO<sub>2</sub>. Water was added to 25 ml and 5 ml of formic acid was added to give a clear solution. Then, 2.8 g of Ca(O<sub>2</sub>CH)<sub>2</sub> and 0.3 g of NaO<sub>2</sub>CH was added with vigorous stirring. The foregoing clear solution did not gel in 1 hour. When dried and fired, this precursor solution would give a biologically active glass having the composition:

SiO<sub>2</sub>—45%  
Na<sub>2</sub>O—24.5%  
CaO—24.5%  
P<sub>2</sub>O<sub>5</sub>—6%.

The precursor solution can be spray-dried and subsequently fired to form spheroidal biologically active glass particles. Alternatively, support particles of alumina, silica, carbon, silica-alumina minerals, titania, clay, calcium silicate, feldspar and zinc oxide, individually or in any combination, can be added to the solution with good agitation. Subsequent drying will produce glass precursor-coated support particles that can be dry-molded and calcined to form shaped biomedical devices. In another alternative, the glass precursor-coated support particles can be treated with an adherent including one or more individual components of biologically active glass and the adhered mass can be molded and fired.

#### EXAMPLE 9

This Example demonstrates generally how one can incorporate certain additives into a solution of precur-

sors for biologically active glass. For instance, Sr, Ba, Li, Al, Fe and/or Ti components can be incorporated into an already prepared aqueous nitric acid solution of precursors. Alternatively, the glass precursors and additive precursors can be formulated in one step into a modified solution of precursors for biologically active glass. The additive components will be present in the nitric acid solution in the form of their nitrates, e.g., as Sr(NO<sub>3</sub>)<sub>3</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, LiNO<sub>3</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub> or as titanyl TiO= ion, respectively. Care should be taken not to mix formic acid/formates with nitric acid/nitrates because of the potential explosive hazard.

#### EXAMPLE 10

Cylindrical  $\alpha$ -alumina pellets of  $\frac{1}{2}$  in. (1.27 cm) in diameter and  $\frac{1}{2}$  in. (1.27 cm) height were washed, dried, and treated with the combined aqueous solution of Example 1, air dried, and fired at 1200° C. The coating, drying, and firing procedures were repeated once and the surfaces were examined using scanning electron microscopy. The fine holes and cracks of the original alumina surface were filled. The surface was smooth and uncrazed.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A stable, aqueous acid solution consisting essentially of precursors that correspond to the components of a biologically active glass, the precursors being convertible to the biologically active glass by heat, the precursor solution showing no substantial amount of precipitation in one hour, the biologically active glass consisting essentially of these components:

SiO<sub>2</sub>, 40 to 62 weight percent;  
Na<sub>2</sub>O, 10 to 32 weight percent;  
CaO, 10 to 32 weight percent;  
CaF<sub>2</sub>, 0 to 18 weight percent;  
P<sub>2</sub>O<sub>5</sub>, 0.1 to 12 weight percent; and  
B<sub>2</sub>O<sub>3</sub>, 0 to 20 weight percent;  
provided that Na<sub>2</sub>O and CaO, taken together, are at least about 30 weight percent.

2. A solution according to claim 1, consisting essentially of precursors that correspond to the components of a biologically active glass consisting essentially of:

SiO<sub>2</sub>, about 40 weight percent;  
Na<sub>2</sub>O, about 24.5 weight percent;  
CaO, about 24.5 weight percent;  
P<sub>2</sub>O<sub>5</sub>, about 6 weight percent; and  
B<sub>2</sub>O<sub>3</sub>, about 5 weight percent.

3. A solution according to claim 1, having a pH less than about 5.

4. A solution according to claim 3, having a pH less than about 4.6.

5. A solution according to claim 4, having a pH less than about 3.8.

6. A solution according to claim 5, wherein the acid is nitric acid.

7. A solution according to claim 5, wherein the acid is formic acid.

8. A solution according to claim 1 wherein the precursors are selected from the group for SiO<sub>2</sub>: Na<sub>2</sub>O(SiO<sub>2</sub>)<sub>3.38</sub>, Na<sub>2</sub>SiO<sub>3</sub>, (NaO)<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>, silicic acid and colloidal SiO<sub>2</sub>;

for Na<sub>2</sub>O: Na<sub>2</sub>O(SiO<sub>2</sub>)<sub>3.38</sub>, Na<sub>2</sub>SiO<sub>3</sub>, (NaO)<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>, Na<sub>3</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, NaNO<sub>3</sub>, Na<sub>3</sub>PO<sub>3</sub>, Na<sub>2</sub>HPO<sub>3</sub>, NaH<sub>2</sub>PO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>O, and Na borates;